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(54) Title: PROCESS FOR DEGRADING ORGANIC SUBSTANCES IN AN AQUEOUS COMPOSITION

(57) Abstract: Process for degrading organic substances in an aqueous composition comprising a step (a) wherein, in a liquid reaction medium, said aqueous composition is reacted with at least one composition comprising hydroxide ions (OH⁻) and hypochlorite in a molar ratio between hydroxide and hypochlorite higher than or equal to 0.001 and lower than 1.5, in order to oxidize said organic substances.



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Process for degrading organic substances in an aqueous composition

The present patent application claims the benefit of the European patent application EP08150925.9 filed on 31 January 2008 and of the European patent application EP 08171544.3 filed on 12 December 2008, the content of both of which is incorporated herein by reference.

5 The present invention is related to a process for degrading substances in an aqueous composition. More specifically it relates to a process for degrading organic substances present in aqueous compositions, by oxidation.

Organic substances are typical contaminants of aqueous effluents originating in chemical processes. Degrading organic contaminants in waste
10 water is a prerequisite before the disposal of such effluent, e.g., before the rejection in environment, since the organic contaminants contributes to the Chemical Oxygen Demand of the effluents, a measure of their oxygen depleting impact on the environment, or when a recycling of the effluent in the chemical process is envisioned.

15 Chlorine is a reactant currently used for degrading organic contaminants in water by oxidation. Such a process is described in US 5,445,741 of SOLVAY DEUTSCHLAND GmbH. Using chlorine as a source of oxidation agent presents however several drawbacks. Chlorine is a toxic gas. It also reacts with organic compounds to substitute chlorine for hydrogen, yielding chlorinated
20 organic compounds, usually both toxic and more difficult to oxidize. It can also lead to undesirable production of chlorates.

The goal of the present invention is to provide a process for degrading organic compounds which does not present the above drawbacks.

In a first embodiment, the invention therefore relates to a process for
25 degrading organic substances in an aqueous composition comprising a step (a) wherein, in a liquid reaction medium, said aqueous composition is reacted with at least one composition comprising hydroxide ions (OH^-) and hypochlorite in a molar ratio between hydroxide and hypochlorite higher than or equal to 0.001 and lower than 1.5, in order to oxidize said organic substances.

30 One of the characteristics of the invention is related to the ratio between hydroxide and hypochlorite in the aqueous composition comprising hydroxide ions and hypochlorite. Without willing to be bound by any theory, it is believed

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that when using such a composition, a good compromise can be obtained between the oxidation rate of the organic substances which is targeted, the chlorination of the organic substances to give chlorinated organic substances highly resistant to oxidation which has to be avoided, and the chlorate formation which has to be avoided.

The aqueous solution containing the organic substances to be degraded will also be referred as the aqueous solution to be treated, subsequently in the description.

The organic substances which are present in the aqueous composition to be treated can be organic aliphatic substances, organic aromatic substances, or mixtures thereof. Those substances can optionally contain at least one heteroatom, selected from halogens, preferably fluorine, chlorine, bromine, iodine, chalcogens, preferably oxygen or sulfur, nitrogen, phosphorus and mixture thereof, and selected more preferably from chlorine, oxygen and mixture thereof.

The aliphatic substances can be cyclic, acyclic, saturated or unsaturated hydrocarbons. Those hydrocarbons are cyclic or acyclic alkanes and alkenes, halogenated cyclic or acyclic alkanes and alkenes, preferably chlorinated, saturated and/or unsaturated aliphatic and/or alicyclic ethers, saturated and/or unsaturated halogenated aliphatic and/or alicyclic ethers, preferably chlorinated, alcohols and halogenated alcohols, preferably chlorinated, ketones and halogenated ketones, preferably chlorinated, aldehydes and halogenated aldehydes, preferably chlorinated, and/or carboxylic acids and halogenated, carboxylic acids, preferably chlorinated.

The aliphatic substances are preferably selected from trichloropropane, preferably 1,2,3-trichloropropane, chloropropenol, preferably 2-chloro-2-propen-1-ol, dichloropropenes, preferably 1,3-dichloropropene cis and 1,3-dichloropropene trans, dichloropropane, preferably 1,3-dichloropropane, dichloropropanols, preferably, 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol, monochloropropanediols, more preferably 2-chloro-1,3-propanediol and 3-chloro-1,2-propanediol, 2-chloro-1-propanol, 1-chloro-2-propanol, chloroethanol, chloroethers, more preferably chloroethers of crude formula $C_6H_{10}Cl_2O_2$, $C_6H_{12}Cl_2O$, $C_6H_9Cl_3O_2$, $C_6H_{11}Cl_3O_2$, acrolein, methyl glycidyl ether, chloroacetone, methanol, glycerol, ethylene glycol, propylene glycol, butane-1,2-diol, hydroxyacetone, glyceraldehyde, formaldehyde, acetaldehyde, acrolein, formic acid, glycolic acid, acetic acid, propionic acid, lactic acid,

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succinic acid, oxalic acid, dichloroacetic acid, glycidol, epichlorohydrin, ethylene oxide, propylene oxide, butylene oxide and mixture thereof.

The aromatic substances comprise at least one ring of aromatic nature. They are preferably halogenated aromatic hydrocarbons comprising at least one
5 ring of aromatic nature and one halogen atom. The halogen may be chosen from fluorine, chlorine, bromine, iodine, and is preferably chlorine. The aromatic ring may be mono or polynuclear and is preferably mononuclear. The aromatic substances are preferably selected from mono-, di-, tri-, tetra-, penta- and hexachloro-benzenes and/or naphthalenes, and mixture thereof. The aromatic
10 substance is preferably monochlorobenzene. The aromatic substance may also be oxygenated like phenol, mono- and polychlorophenol, preferably phenol.

The content of the organic substance in the aqueous composition to be treated is usually such that the total organic carbon (TOC) of the aqueous composition to be treated is higher than or equal to 0.1 g C/kg, preferably higher
15 than or equal to 0.5 g C/kg and more preferably higher than or equal to 1 g C/kg. That TOC is usually lower than or equal to 20 g C/kg, preferably lower than or equal to 10 g C/kg and more preferably lower than or equal to 5 g C/kg.

The content of the organic substance in the aqueous composition to be treated is usually such that the chemical oxygen demand (COD) of the aqueous composition to be treated is higher than or equal to 0.25 g O/kg, preferably
20 higher than or equal to 1.25 g O/kg and more preferably higher than or equal to 2.5 g O/kg. That COD is usually lower than or equal to 50 g O/kg, preferably lower than or equal to 25 g O/kg and more preferably lower than or equal to 15 g O/kg.

25 The aqueous composition to be treated generally contains inorganic compounds, like salts for instance. The salts can be organic salts, inorganic salts or mixture thereof. The inorganic salts are preferred. Inorganic salts are salts for which the constitutive cations and anions do not contain any carbon-hydrogen bond and any carbon-heteroatom bond with the exception of carbon-oxygen
30 bonds. Metal cyanides, for instance, are not considered as inorganic salts. The inorganic salts are selected from alkaline or alkaline-earth chlorides, sulfates, hydrogen sulfates, hydroxides, carbonates, hydrogen carbonates, phosphates, hydrogen phosphates, borates and any mixture thereof, preferably from alkaline or alkaline-earth chlorides, more preferably from sodium and potassium chloride
35 and the salt is most preferably sodium chloride. Aqueous solutions containing

sodium chloride are also known as brines. The aqueous solution to be treated according to the process of the invention is often a brine.

The salt content of the aqueous composition to be treated is usually higher than or equal to 5 g/kg, often higher than or equal to 10 g/kg, frequently higher than or equal to 20 g/kg, commonly higher than or equal to 30 g/kg of composition to be treated, preferably higher than or equal to 50 g/kg, more preferably higher than or equal to 100 g/kg, still more preferably higher than or equal to 140 g/kg, yet more preferably higher than or equal to 160 g/kg and most preferably higher than or equal to 200 g/kg. That salt content is usually lower than or equal to 270 g/kg of composition to be treated, preferably lower than or equal to 250 g/kg and most preferably lower than or equal to 230 g/kg.

The aqueous solution to be treated can originate from any process, preferably from processes generating brines contaminated by organic substances. Those are for instance processes for manufacturing epoxides, preferably ethylene oxide, propylene oxide, butylene oxide or epichlorohydrin, processes for manufacturing chlorinated organic compounds, preferably dichloroethane, processes for manufacturing mono- and polyisocyanates, preferably 4,4'-methylenediphenyl diisocyanate (MDI) or toluene diisocyanate (TDI) or hexamethylen-1,6-diisocyanate (HDI). The aqueous composition to be treated can be a mixture of aqueous compositions originating from at least two different manufacturing processes.

The aqueous composition containing the organic substances to be treated originates preferably from a process for manufacturing an epoxide, more preferably for manufacturing an epoxide from glycerol, and most preferably for manufacturing epichlorohydrine from glycerol or from a process for manufacturing a chlorinated organic compound, preferably 1,2-dichloroethane, or from both processes.

The composition containing hypochlorite can be a solid, a solution or a suspension. It is preferably a solid or a solution, and more preferably a solution.

The expression hypochlorite is here intended to designate any compound selected from hypochlorous acid (HOCl), a salt from hypochlorous acid, or a mixture thereof.

The salt from hypochlorous acid can be an organic salt, an inorganic salt or a mixture thereof. This salt is preferably an inorganic salt, preferably selected from ammonium hypochlorite, metal salts of hypochlorite and mixture thereof, more preferably selected from alkaline and alkaline-earth metal hypochlorite,

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and mixture thereof, still more preferably selected from sodium and calcium hypochlorite, and mixture thereof and this salt is most preferably sodium hypochlorite.

5 The aqueous composition containing hypochlorite is preferably a solution containing sodium hypochlorite.

The aqueous composition containing hypochlorite and hydroxide ions may in addition contain chlorate.

The expression chlorate is here intended to designate any compound selected from chloric acid (HClO_3), a salt from chloric acid, or a mixture thereof.

10 The salt from chloric acid can be an organic salt, an inorganic salt or a mixture thereof. This salt is preferably an inorganic salt, preferably selected from ammonium chlorate, metal salts of chlorate and mixture thereof, more preferably selected from alkaline and alkaline-earth metal chlorate, and mixture thereof, still more preferably selected from sodium and calcium chlorate, and mixture thereof and this salt is most preferably sodium chlorate.

15 The aqueous composition containing hypochlorite and hydroxide ions is preferably a solution containing sodium chlorate.

The chlorate molar content of the aqueous composition containing chlorate, hypochlorite and hydroxide ions is usually higher than or equal to 0.1 mmol chlorate/kg, often higher than or equal to 1 mmol/kg, frequently higher than or equal to 2 mmol/kg and more specifically higher than or equal to 5 mmol/kg. That content is usually lower than or equal to 100 mmol chlorate/kg, often lower than or equal to 50 mmol/kg, frequently lower than or equal to 20 mmol/kg and more specifically lower than or equal to 10 mmol/kg.

25 The aqueous composition containing hypochlorite also contains hydroxide ions OH^- in a molar ratio between hydroxide and hypochlorite ($[\text{OH}^-] / [\text{ClO}^-]$) higher than or equal to 0.001 and lower than to 1.5. The molar content of hypochlorite ($[\text{ClO}^-]$) is here intended to designate the sum of the molar contents of hypochlorous acid and salt of hypochlorous acid in the aqueous composition containing hypochlorite. That molar ratio ($[\text{OH}^-]/[\text{ClO}^-]$) is preferably higher than or equal to 0.01 and more preferably higher than or equal to 0.05, still more preferably higher than or equal to 0.1, yet more preferably higher than or equal to 0.2 and most preferably higher than or equal to 0.75. That molar ratio is preferably lower than or equal to 1.4, more preferably lower than or equal to 1.2 and most preferably lower than or equal to 1.0.

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The aqueous composition containing hypochlorite and hydroxide ions can contain other compounds, like a salt different from the hypochlorous acid salt. That salt can be an organic salt, an inorganic salt or a mixture thereof. The salt is preferably an inorganic salt, preferably selected alkaline or alkaline-earth chlorides, sulfates, hydrogen sulfates, carbonates, hydrogen carbonates, phosphates, hydrogen phosphates, borates and any mixture thereof, preferably from alkaline or alkaline-earth chlorides, more preferably from sodium and potassium chloride and the salt is most preferably sodium chloride. This salt usually results from the process used for preparing the aqueous composition containing hypochlorite.

The salt content, not including the possible salt of hypochlorous acid, of the aqueous composition containing hypochlorite and hydroxide ions is usually higher than or equal to 30 g/kg of composition to be treated, preferably higher than or equal to 50 g/kg, more preferably higher than or equal to 100 g/kg, still more preferably higher than or equal to 140 g/kg, yet more preferably higher than or equal to 160 g/kg and most preferably higher than or equal to 200 g/kg. That salt content is usually lower than or equal to 270 g/kg of composition to be treated, preferably lower than or equal to 250 g/kg and most preferably lower than or equal to 230 g/kg.

The aqueous composition containing hypochlorite and hydroxide ions can be obtained by any means, preferably by dissolving gaseous chlorine in water containing a basic compound like for instance, ammonium hydroxide, an alkaline hydroxide, an alkaline earth hydroxide, or a mixture thereof. Water containing a sodium hydroxide or a calcium hydroxide or a mixture thereof is preferred and water containing sodium hydroxide is more preferred.

The hypochlorite molar content of the aqueous composition containing hypochlorite and hydroxide ions is usually higher than or equal to 0.1 mol hypochlorite/kg, preferably higher than or equal to 0.5 mol/kg, more preferably higher than or equal to 1 mol/kg and most preferably higher than or equal to 1.3 mol/kg. That content is usually lower than or equal to 5 mol hypochlorite/kg, preferably lower than or equal to 3 mol/kg, more preferably lower than or equal to 2 mol/kg and most preferably lower than or equal to 1.7 mol/kg.

The amount of the aqueous composition containing hypochlorite and hydroxide ions added to the aqueous composition to be treated is usually such that the molar ratio between the hypochlorite added and the COD (expressed in

mol of O) of the aqueous composition to be treated, before reaction, is higher than or equal to 1, preferably higher than or equal to 1.2 and most preferably higher than or equal to 1.4. That amount is usually such that the molar ratio between the hypochlorite added and the COD (expressed in mol of O) of the aqueous composition to be treated, before reaction, is lower than or equal to 8, preferably lower than or equal to 4 and most preferably lower than or equal to 3.

The liquid reaction medium may be a single-phase or multi-phase medium.

The liquid reaction medium is composed of all of the dissolved or dispersed solid compounds, dissolved or dispersed liquid compounds and dissolved or dispersed gaseous compounds at the temperature and pressure of the reaction. The liquid reaction medium is preferably a multi-phase medium.

The process according to the invention can be carried out in a discontinuous, continuous or semi-continuous mode. The continuous mode is preferred. By continuous mode, one intends to denote a mode wherein the aqueous composition to be treated and the composition comprising hydroxide ions and hypochlorite are continuously fed to the process and wherein the liquid reaction medium is continuously withdrawn from the process. By discontinuous mode, one intends to denote any other mode. The semi-continuous mode can be considered as a discontinuous mode. By the term continuously, one intends to denote without substantial interruption.

In the process according to the invention, the pH at which the reaction of step (a) is carried out is preferably controlled. That pH is preferably controlled and maintained in a given range. The lowest limit of the pH range is generally higher than or equal to 6, preferably higher than or equal to 7 and most preferably higher than or equal to 8. The highest limit of the pH range is generally lower than or equal to 11, preferably lower than or equal to 10 and most preferably lower than or equal to 9. The pH has to be maintained at such set values since pH changes occur during the course of the oxidation reaction. The pH values are given for the reaction conditions of step (a), *i.e.*, temperature, pressure and ionic strength.

In order to maintain the pH in a given range, the pH is measured and adjusted if necessary.

The pH measurement can be done either continuously or periodically. In this last case, the measurement is usually carried out at a frequency sufficiently high to maintain the pH in the set range during at least 80 % of the duration of

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step (a) of the process, often during at least 90 %, frequently during at least 95 % and in particular during at least 99 %.

The pH measurement can be carried out “in situ” in the reaction medium under the reaction conditions or “ex situ” in a sample withdrawn from the reaction medium and brought to an adequate temperature and an adequate pressure to assure a good longevity to the pH measurement equipment. A temperature 25°C and a pressure of 1 bar are examples of adequate temperature and pressure.

The pH measurement can be carried out by any means. Measurement with a pH sensitive electrode is convenient. Such an electrode should be stable in the reaction medium under the reaction conditions and should not contaminate the reaction medium. Glass electrodes for measuring pH are more particularly convenient. Examples of such electrodes are given in Ullmann’s Encyclopedia of Industrial Chemistry,[®] 2005, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 10.1002/14356007.e19_e01, pp. 8-15. Electrodes of the type 405-DPAS-SC-K85 supplied by METTLER TOLEDO[®] or of the types Ceragel CPS71 and Orbisint CPS11 supplied by ENDRESS + HAUSER[®] are examples of electrodes that can be used.

The pH can be adjusted and maintained at said values either by addition of an acidic compound or by addition of a basic compound. Any acidic or basic compounds can be used to maintain the pH. Inorganic acids and inorganic bases are preferred. Hydrogen chloride, gaseous and/or in aqueous solution, is a more preferred acidic compound. Sodium or calcium hydroxides, solids and/or in aqueous solution and/or suspensions, are more preferred basic compounds, with sodium hydroxide aqueous solutions being most preferred.

The adjustment can be carried out in an automated or in a non-automated mode. It is preferred to use an automated mode wherein the control of the pH is exerted by a closed circuit known as control loop. Such control loops are described in Ullmann’s Encyclopedia of Industrial Chemistry,[®] 2005, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 10.1002/14356007.e19_e01, pp.24-27. A PROMINENT[®] DULCOMETER[®] system type PHD is an example of an automated pH control and adjustment apparatus that can be used.

In the process according to the invention, the temperature at which the reaction of step (a) is carried out, is usually higher than or equal to 10°C, preferably higher than or equal to 30°C, more preferably higher than or equal

to 60°C and most preferably higher than or equal to 80°C. That temperature is usually lower than or equal to 200°C, preferably lower than or equal to 180°C, more preferably lower than or equal to 160°C and most preferably lower than or equal to 135°C.

5 In the process according to the invention, the reaction of step (a) can be carried out under a pressure of 1 bar absolute, under a pressure above 1 bar absolute or under a pressure below 1 bar absolute. It is preferred to carry out the reaction of step (a) under a pressure that is regulated or set between 1 and 11 bar absolute, more preferably under a pressure of 1.1 to 7 bar and most preferably
10 under a pressure of 1.1 to 4 bar.

 It is preferred to carry out the reaction at the boiling temperature of the liquid reaction medium. Such a procedure has the advantage of allowing the removal of heat sensitive and/or volatile compounds formed during the reaction, for instance bicarbonate, carbonic acid and carbon dioxide.

15 In the process according to the invention, when step (a) of the process is carried out in a discontinuous mode, the duration of the reaction of step (a) is generally higher than or equal to 0.05 h, preferably higher than or equal to 0.1 h, more preferably higher than or equal to 0.2 h and most preferably higher than or equal to 0.5 h. That duration is usually lower than or equal to 8 h, preferably
20 lower than or equal to 4 h, more preferably lower than or equal to 2 h and most preferably lower than or equal to 1 h. The duration is counted from the time of addition of the composition containing hypochlorite to the aqueous solution to be treated.

 In the process according to the invention, when step (a) of the process is
25 carried out in a continuous mode, the residence time of the reaction of step (a) is usually higher than or equal to 0.05 h, preferably higher than or equal to 0.1 h, more preferably higher than or equal to 0.2 h and most preferably higher than or equal to 0.5 h. That residence time is usually lower than or equal to 8 h, preferably lower than or equal to 4 h, more preferably lower than or equal to 2 h
30 and most preferably lower than or equal to 1 h. The residence time is defined by the ratio between the volume of the liquid reaction medium and the flow of the liquid reaction medium.

 In the process according to the invention, the reaction of step (a) can be carried out in one or more reaction zones, preferably in at least two reaction
35 zones and more preferably in at least three reaction zones. The reactions zones may be composed of volumes assembled in a single jacket or volumes in

separate jackets. In the case where the volumes are assembled in a single jacket, the reaction zones may be positioned horizontally or vertically with respect to one another. In any case, the transfer from one zone to another may take place by gravity or by forced circulation. These reaction zones may be placed in any configuration, in series, in parallel or some in series and others in parallel. These reactions zones can be operated under any type of regime, like for instance, mixed regime, preferably perfectly mixed regime or plug flow regime. It is preferred that at least one of the zone is operated under mixed regime, preferably perfectly mixed regime and at least another one is operated under plug flow regime, and it is more preferred that the zone operating under plug flow regime is located after the zone operating under mixed regime, preferably perfectly mixed regime. Such conditions are especially well suited when the process is carried out under continuous mode.

In the process according to the invention, the reaction zones may be supplied independently of one another, with the aqueous composition to be treated, with the aqueous composition containing the hypochlorite, with any other compositions, or with at least two of these compositions. The other composition may comprise for instance the acidic or the basic compound used to adjust the pH of the liquid reaction medium, or a stripping gas to remove volatile reactions products. When several reaction zones are in series, it is preferred to supply the totality or the major part of the aqueous composition containing the hypochlorite in the first reaction zone of the series. Some additional minor parts of the aqueous composition containing the hypochlorite can be added in the next zones of the series. The pH of the liquid reaction medium is preferably adjusted independently in the different reaction zones of the series.

The expression "reaction zones" is understood to mean zones where all the conditions needed for the oxidation reaction are found.

The aqueous composition obtained after the reaction of step (a) exhibits usually reduced COD and TOC levels.

The TOC of the aqueous composition after the reaction step is usually lower than or equal to 100 mg C/kg, preferably lower than or equal to 60 mg C/kg and more preferably lower than or equal to 20 mg C/kg. That TOC is usually higher than or equal to 0.1 mg C/kg.

The COD of the aqueous composition after the reaction step is usually lower than or equal to 250 mg O/kg, preferably lower than or equal

to 150 mg O/kg and more preferably lower than or equal to 50 mg O/kg. That COD is usually higher than or equal to 1 mg O/kg.

The compounds responsible for the COD and TOC in the aqueous composition after the reaction of step (a) may be selected from the organic compounds present in the aqueous composition to be treated mentioned above and that have not been oxidized, but also selected from the group consisting of carboxylic acids, aldehydes, ketones or any mixtures thereof.

The carboxylic acid is preferably selected from the group consisting of monocarboxylic, polycarboxylic acids, and mixtures thereof. The monocarboxylic acid and the polycarboxylic acids contain usually from 1 to 10 carbon atoms. The carboxylic acids can contain hetero atoms in their molecule. Oxygen, sulfur, halogens and nitrogen are examples of such heteroatoms. The monocarboxylic acid is more preferably selected from the group consisting of formic acid, acetic acid, dichloroacetic acid, propionic acid, butyric acid, glycolic acid, lactic acid and any mixture thereof. The polycarboxylic acid is more preferably selected from the group consisting of oxalic acid, succinic acid, adipic acid, and any mixture thereof.

The ketone is usually selected from the group consisting of acetone, hydroxyacetone, dihydroxyacetone and mixture thereof. The ketone is often hydroxyacetone.

The aldehydes are preferably selected from the group consisting of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, glyceraldehyde, acrolein, and any mixture thereof.

The aqueous composition obtained after the reaction of step (a) exhibits usually a chlorate ($[\text{ClO}_3^-]$) content which is usually lower than or equal to 200 mmol ClO_3^-/kg , preferably lower than or equal to 100 mmol ClO_3^-/kg and more preferably lower than or equal to 50 mmol ClO_3^-/kg . That chlorate content is usually higher than or equal to 0.01 mmol ClO_3^-/kg . The molar content of chlorate ($[\text{ClO}_3^-]$) is here intended to designate the sum of the molar contents of chloric acid and salt of chloric acid in the aqueous composition.

The aqueous composition obtained after the reaction of step (a) exhibits usually a hypochlorite ($[\text{ClO}^-]$) content which is usually lower than or equal to 100 mmol ClO^-/kg , preferably lower than or equal to 50 mmol ClO^-/kg and more preferably lower than or equal to 20 mmol ClO^-/kg . That hypochlorite content is usually higher than or equal to 0.001 mmol ClO^-/kg .

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The aqueous composition obtained after the reaction step exhibits usually a salt content, preferably an inorganic salt, preferably selected from alkaline or alkaline-earth chlorides, sulfates, hydrogen sulfates, carbonates, hydrogen carbonates, phosphates, hydrogen phosphates, borates, chlorates, hypochlorites and any mixture thereof, more preferably from alkaline or alkaline-earth chlorides, still more preferably from sodium and potassium chloride and most preferably from sodium chloride, usually higher than or equal to 30 g/kg of composition obtained after the reaction step, preferably higher than or equal to 50 g/kg, more preferably higher than or equal to 100 g/kg, still more preferably higher than or equal to 140 g/kg, yet more preferably higher than or equal to 160 g/kg and most preferably higher than or equal to 200 g/kg. That salt content is usually lower than or equal to 270 g/kg of composition, preferably lower than or equal to 250 g/kg and most preferably lower than or equal to 230 g/kg.

The aqueous composition obtained after the reaction step can be used as such as a starting material in an electrolysis process, preferably in an electrolysis process for producing chlorine.

In a second embodiment, the aqueous composition containing the organic substances contains at least one salt and the process for degrading organic substances in the aqueous composition comprises a further step (b1), wherein, at least part of the reaction medium of step (a) is subjected to an operation selected from the group consisting of cooling, evaporative crystallization, and any combination thereof, in order to precipitate at least part of the salt, followed by a step wherein at least part of the precipitated salt and at least part of the water present in the aqueous composition are recovered.

In a first variant of the second embodiment, the operation is a cooling operation. This operation consists of setting and maintaining the temperature of the reaction medium of step (a) to a temperature lower than the temperature of the reaction of step (a). That temperature is generally lower than 25°C, often lower than or equal to 10°C, frequently lower than or equal to 0°C and in particular lower than -10°C. That temperature is generally higher than or equal to -22°C and often higher than or equal to -20°C.

The cooling operation can be carried out in a continuous or discontinuous mode. The continuous mode is preferred.

When the cooling operation is carried out under the discontinuous mode, the duration of the cooling operation is usually higher than or equal to 1 min,

often higher than or equal to 10 min and frequently higher than or equal to 20 min. That duration is usually lower than or equal to 6 h, often lower than or equal to 3 h and frequently lower than or equal to 2 h.

When the cooling operation is carried out under the continuous mode, the residence time of the cooling operation is usually higher than or equal to 1 min, often higher than or equal to 10 min and frequently higher than or equal to 20 min. That residence time is usually lower than or equal to 6 h, often lower than or equal to 3 h and frequently lower than or equal to 2 h.

The pressure at which the cooling operation is carried out, is usually higher than or equal to 0.1 bar, often higher than or equal to 0.5 bar and frequently higher than or equal to 0.9 bar. That pressure is usually lower than or equal to 10 bar, often lower than or equal to 5 bar and frequently lower than or equal to 2 bar.

This operation is usually carried out when the concentration of the salt in the reaction medium of step (a) is high, *i.e.* higher than or equal to 230 g/kg, in particular higher than or equal to 240 g/kg and more particularly higher than or equal to 250 g/kg.

This operation can be carried out at the pH of the reaction medium of step (a) as such or at a modified pH. The operation is preferably carried out after acidification to a pH lower than 5 to eliminate carbonate salts. The pH is then possibly adjusted to a higher value before or during the precipitation. The pH can be modified or adjusted either by addition of an acidic compound or by addition of a basic compound. Any acidic or basic compounds can be used to maintain the pH. Inorganic acids and inorganic bases are preferred. Hydrogen chloride, gaseous and/or in aqueous solution, is a more preferred acidic compound. Sodium or potassium hydroxides, solids and/or in aqueous solution and/or suspensions, are more preferred basic compounds, with sodium hydroxide aqueous solutions being most preferred.

In a second variant of the second embodiment, the operation is a evaporative crystallization operation.

The term "evaporative crystallization" is intended to denote a process resulting in the crystallization of a compound by removing, by evaporation, a compound which promotes its dissolution in the medium. This process is described in "Perry's Chemical Engineers' Handbook" in the 11th section of the 7th edition, 1997.

The temperature at which the evaporative crystallization is carried out is generally higher than 20°C, usually higher than or equal to 40°C, often higher than or equal to 60°C and frequently higher than or equal to 90°C. That temperature is generally lower than or equal to 200°C and often lower than or equal to 150°C.

The evaporative crystallization can be carried out at the pH of the reaction medium of step (a) as such or at a modified pH. The operation is preferably carried out after acidification to a pH lower than 5 to eliminate carbonate salts. The pH is then possibly adjusted to a higher value before or during the precipitation. The pH can be modified or adjusted either by addition of an acidic compound or by addition of a basic compound. Any acidic or basic compounds can be used to maintain the pH. Inorganic acids and inorganic bases are preferred. Hydrogen chloride, gaseous and/or in aqueous solution, is a more preferred acidic compound. Sodium or potassium hydroxides, solids and/or in aqueous solution and/or suspensions, are more preferred basic compounds, with sodium hydroxide aqueous solutions being most preferred.

The evaporative crystallization operation can be carried out in a discontinuous or continuous mode. The continuous mode is preferred.

When the evaporative crystallization operation is carried out under the discontinuous mode, the duration of the operation is usually higher than or equal to 1 min, often higher than or equal to 10 min and frequently higher than or equal to 20 min. That duration is usually lower than or equal to 6 h, often lower than or equal to 3 h and frequently lower than or equal to 2 h.

When the evaporative crystallization operation is carried out under the continuous mode, the residence time of the operation is usually higher than or equal to 1 min, often higher than or equal to 10 min and frequently higher than or equal to 20 min. That duration is usually lower than or equal to 6 h, often lower than or equal to 3 h and frequently lower than or equal to 2 h.

The pressure at which the evaporative crystallization operation is carried out, is generally higher than or equal to 0.001 bar absolute. This pressure is generally lower than or equal to 15 bar, usually lower than or equal to 4 bar often lower than or equal to 1 bar, frequently lower than or equal to 0.5 bar and more specifically lower than or equal to 0.1 bar.

This operation is usually carried out when the concentration of the salt in the reaction medium of step (a) is low, *i.e.* lower than or equal to 270 g/kg, in

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particular lower than or equal to 250 g/kg and more particularly lower than or equal to 230 g/kg.

In the first variant of the second embodiment, a solid is generally precipitated in the reaction medium submitted to the cooling operation. The reaction medium can be further submitted to a separation operation in order to
5 recover at least one solid and at least one aqueous residue.

The separation operation can be selected from the group consisting of decantation, filtration, centrifugation, and any combination of at least two of them. The separation operation may contain a washing of the separated solid.
10 This washing can be carried out with any liquid. Water is preferred, deionized water is more preferred and distilled water is most preferred. A filtration operation is preferred.

The recovered solid comprises at least one salt. The salt is preferably an inorganic salt, preferably selected from the group consisting of alkaline or
15 alkaline-earth chlorides, sulfates, hydrogen sulfates, carbonates, hydrogen carbonates, phosphates, hydrogen phosphates, borates and any mixture thereof, more preferably from alkaline and alkaline-earth chlorides, still more preferably from sodium and potassium chloride and the salt is most preferably sodium chloride.

The recovered solid is usually a crystalline solid, *i.e.*, a solid of which the X-ray diffraction pattern exhibits well defined diffraction lines.

The salt content of the solid is usually higher than or equal to 300 g/kg, commonly higher than or equal to 400 g/kg, in many cases higher than or equal to 500 g/kg, often higher than or equal to 550 g/kg, frequently higher than or
25 equal to 590 g/kg, specifically higher than or equal to 600 g/kg and in particular higher than or equal to 610 g/kg.

The recovered solid may comprise organic substances. These substances can be those already present in the aqueous composition to be treated, like as defined above, or organic substances formed during the reaction of step (a). The
30 TOC of the recovered solid is usually lower than or equal to 10 mg C/kg, preferably lower than or equal to 5 mg C/kg and more preferably lower than or equal to 2 mg C/kg. That TOC is usually higher than or equal to 0.1 mg C/kg.

The separation operation can be carried out in a continuous or discontinuous mode. The continuous mode is preferred.

The recovered solid can be disposed off or used in solution preparation
35 and/or in solution resaturation, for use in an electrolysis process. This is

particularly the case when the solid consists essentially of sodium chloride and is used for brine preparation and/or resaturation.

The recovered aqueous residue can be disposed off, send to a biological treatment, recycled to the treatment of step (b1), recycled to the treatment of the first variant and any combination of at least two of these operations.

In the second variant of the second embodiment, one usually obtains at least one evaporate and at least one evaporation residue.

The evaporate comprises water as the major component. The water content is usually higher than or equal to 900 g/kg, commonly higher than or equal to 950 g/kg, in many cases higher than or equal to 990 g/kg, often higher than or equal to 995 g/kg, frequently higher than or equal to 999 g/kg, specifically higher than or equal to 999.9 g/kg and in particular higher than or equal to 999.99 g/kg. That content is usually lower than or equal to 99.999 g/kg.

The evaporate may comprise a salt, often an inorganic salt. The salt content is usually lower than or equal to 1 g/kg, commonly lower than or equal to 0.5 g/kg, in many cases lower than or equal to 0.1 g/kg, often lower than or equal to 0.05 g/kg, frequently lower than or equal to 0.01 g/kg, specifically lower than or equal to 0.005 g/kg and in particular lower than or equal to 0.001 g/kg. That content is usually higher than or equal to 0.001 mg/kg.

The evaporate may comprise organic substances. These substances can be those already present in the aqueous composition to be treated, like as defined above, or organic substances formed during the reaction of step (a). The TOC of the evaporate is usually lower than or equal to 10 mg C/kg, preferably lower than or equal to 5 mg C/kg and more preferably lower than or equal to 2 mg C/kg. That TOC is usually higher than or equal to 0.1 mg C/kg.

The evaporate residue generally comprises at least one solid and at least one aqueous phase. This residue can be further submitted to a separation operation in order to recover at least one solid and at least one aqueous residue.

The separation operation and the characteristics of the recovered solid are as described hereabove for the first variant of the second embodiment except that the salt content of the solid is usually higher than or equal to 900 g/kg, commonly higher than or equal to 950 g/kg, in many cases higher than or equal to 980 g/kg, often higher than or equal to 990 g/kg, frequently higher than or equal to 999 g/kg, specifically higher than or equal to 999.5 g/kg and in particular higher than or equal to 999.9 g/kg.

The aqueous residue is usually more concentrated in organic substances than the aqueous composition submitted to the treatment of step (b1). These substances can be those already present in the aqueous composition to be treated, like as defined above or organic substances formed during the reaction of step (a). The TOC of the aqueous residue is usually higher than or equal to 50 mg C/kg, generally higher than or equal to 100 mg C/kg, in many cases higher than or equal to 200 mg C/kg, often higher than or equal to 400 mg C/kg and frequently higher than or equal to 600 mg C/kg.

That recovered aqueous residue can be disposed off, send to a biological treatment, recycled to the treatment of the second variant, recycled to the treatment of the first variant and any combination of at least two of these operations.

The recovered solid and/or the evaporate can be disposed off or used in solution preparation and/or in solution resaturation, for use in an electrolysis process. This is particularly the case when the solid consists essentially of sodium chloride and is used for brine preparation and/or saturation.

The use of the evaporate has the advantage of requiring no extra water which is especially important for processes, like electrolysis processes located in countries with limited water supply.

Further variants of the second embodiment can be obtained by combining in any way the treatments of the first and the second variants.

In a third embodiment, step (a) of the process according to the invention is carried out at a first pH value and the process for degrading organic substances in an aqueous composition comprises a further step (b2), wherein, at least part of the reaction medium of step (a) is subjected to an acidification operation in order to bring the pH at a second value lower than the pH value of step (a) and the organic substances are further oxidized.

Without willing to be bound by any theory, it is believed that the two step process of the third embodiment allows a high organic substances degradation level for the following reasons :

- At the higher pH of step (a), the oxidation of the organic substances proceed at a slower rate but the chlorination of the organic substances to give chlorinated organic substances highly resistant to oxidation is disfavored
- At the lower pH of step (b2), the oxidation of the remaining organic substances is more rapid and the chlorination of those remaining organic substances is reduced due to their lower concentration.

In other words, it is better to carry out step (b2) on an aqueous composition with a reduced Total Organic Content.

In that embodiment, the reaction of step (b2) is carried out at a pH controlled and maintained in a given range. The lowest limit of that pH range is generally higher than or equal to 0.01, preferably higher than or equal to 1, more preferably higher than or equal to 2 and most preferably higher than or equal to 3. The highest limit of that pH range is generally lower than 6, preferably lower than or equal to 5.5, more preferably lower than or equal to 5 and most preferably lower than or equal to 4. The pH has generally to be maintained at such set values since pH changes occur during the course of the oxidation reaction. The pH can be maintained at said values either by addition of an acidic compound or by addition of a basic compound. The acidic operation can be carried out by adding an acidic compound to the reaction medium from step (a), as the one described above.

In that embodiment, the temperature at which the reaction of step (b2) is carried out, is usually higher than or equal to 10°C, preferably higher than or equal to 30°C, more preferably higher than or equal to 60°C and most preferably higher than or equal to 80°C. A temperature higher than or equal to 90°C is convenient. A temperature higher than or equal to 100°C suits well. That temperature is usually lower than or equal to 200°C, preferably lower than or equal to 180°C, more preferably lower than or equal to 160°C and most preferably lower than or equal to 135°C. A temperature lower than or equal to 120°C is convenient. A temperature lower than or equal to 110°C suits well.

In the process according to the invention, the reaction of step (b2) is usually carried out under a pressure of 1 bar absolute, under a pressure above 1 bar absolute or under a pressure below 1 bar absolute. It is preferred to carry out the oxidation operation under a pressure that is regulated or set between 1 and 11 bar absolute, more preferably under a pressure of 1.1 to 7 bar and most preferably under a pressure of 1.1 to 4 bar.

In the process according to the invention, when step (b2) of the process is carried out in a discontinuous mode, the duration of the reaction of step (b2) is usually higher than or equal to 0.05 h, preferably higher than or equal to 0.1 h, more preferably higher than or equal to 0.2 h and most preferably higher than or equal to 0.5 h. That duration is usually lower than or equal to 8 h, preferably lower than or equal to 4 h, more preferably lower than or equal to 2 h and most

preferably lower than or equal to 1 h. The duration is counted from the time of pH change of the reaction medium arising from step (a) to be treated.

In the process according to the invention, when step (b2) of the process is carried out in a continuous mode, the residence time of the reaction of step (b2) is usually higher than or equal to 0.05 h, preferably higher than or equal to 0.1 h, more preferably higher than or equal to 0.2 h and most preferably higher than or equal to 0.5 h. That residence time is usually lower than or equal to 8 h, preferably lower than or equal to 4 h, more preferably lower than or equal to 2 h and most preferably lower than or equal to 1 h. The residence time is defined by the ratio between the volume of the liquid reaction medium and the flow of the liquid reaction medium.

The reaction of step (b2) can be carried in one or more reaction zones, as described for the reaction of step (a).

In a first variant of the third embodiment, no additional compounds are added to step (b2) except the acidic compound if necessary to lower the pH, and the acidic or the basic compounds used if necessary to regulate the pH of step (b2). Without willing to be tied by any theory, it is believed that at such a pH, the chlorates ions and/or the active chlorine which are present in the reaction mixture at the end of step (a) are able to oxidize the remaining organic compounds, for instance carboxylic acids still present in the reaction medium after step (a) of the process.

The expression "active chlorine" is understood to mean molecular chlorine and its reaction products with water, chloride ions or with a basic agent, such as hypochlorous acid, trichloride ion and sodium hypochlorite for example. The content of active chlorine can be expressed in g of Cl_2/kg or mol of Cl_2/kg .

In a second variant of the third embodiment, at least one compound is added to step (b2) in addition to the acidic compound if necessary to lower the pH, and the acidic or the basic compounds used if necessary to regulate the pH of step (b2). That compound can be selected from the group consisting of chlorine, oxygenated chlorine compounds, and any mixture thereof. The oxygenated chlorine compound can be selected from the group consisting of hypochlorite, chlorate, chlorine dioxide, dichlorine monoxide, and any mixture thereof. The hypochlorite can be as described above. The chlorine can liquid or gaseous, preferably gaseous. It can be use pure or diluted by any inert gas like nitrogen, for instance. The chlorine dioxide is generally used as a gas. It can be produced *in situ* by addition of chlorine and chlorite (ClO_2^-).

In a first aspect of the first variant of that third embodiment, the pH is maintained at a value higher than or equal to 2 and lower than 6, preferably at a value higher than or equal to 3 and lower than or equal to 5.

5 In a second aspect of the first variant of that third embodiment, the pH is maintained at a value higher than or equal to 0.01 and lower than 3, preferably at a value higher than or equal to 0.01 and lower than 2.

In a first aspect of the second variant of that third embodiment, the additional compound is selected from the group consisting of chlorine, oxygenated chlorine compounds, and any mixture thereof, and the pH is
10 maintained at a value higher than or equal to 2 and lower than 6, preferably at a value higher than or equal to 3 and lower than or equal to 5. Oxygenated chlorine compounds can be selected from the group consisting of hypochlorite, chlorate, chlorine dioxide, dichlorine monoxide, and any mixture thereof.

In a second aspect of the second variant of that third embodiment, the
15 additional compound is selected from the group the group consisting of chlorine, oxygenated chlorine compounds, and any mixture thereof, and the pH is maintained at a value higher than or equal to 0.01 and lower than 3, preferably at a value higher than or equal to 0.01 and lower than 2. Oxygenated chlorine compounds can be selected from the group consisting of hypochlorite, chlorate,
20 chlorine dioxide, dichlorine monoxide, and any mixture thereof.

In the first and third embodiments, the partial pressure of chlorine is generally higher than or equal to 0.001 bar, often higher than or equal to 0.01 bar, frequently higher than or equal to 0.1 bar and in particular higher than or equal to 0.5 bar. The partial pressure of chlorine is generally lower than
25 or equal to 10 bar, often lower than or equal to 5 bar, frequently lower than or equal to 3 bar and in particular lower than or equal to 2 bar.

The partial pressure of chlorine is as defined above more particularly in the first and second aspects in the second variant of the third embodiment.

In a third variant of the third embodiment, during step (b2) a treatment
30 with UV (Ultra Violet)-visible light is carried out on the reaction medium. That third variant will be referred hereafter as a chloro-photolysis treatment.

The wavelength of the UV-visible light used is generally higher than or equal to 100 nm, often higher than or equal to 150 nm and frequently higher than or equal to 200 nm. That wavelength is generally lower than or equal to 600 nm,
35 often lower than or equal to 500 nm, frequently lower than or equal to 400 nm and in particular lower than or equal to 300 nm. The variation of the light

intensity over the wavelength spectrum of the UV-visible light used can be continuous or discontinuous. UV-visible light with a discontinuous spectrum of wavelength is often used.

5 The UV-visible light used in that third aspect can be produced by any source, like UV-visible lamps for instance. Medium pressure UV lamps like High Tech DQ or QC from Heraeus-Noblelight are examples of such sources.

10 In that third variant the ratio between the electrical energy consumed by the source in Wh and the volume of the treated part of the reaction medium of step (a) in liter is usually higher than or equal to 1 Wh/l, often higher than or equal to 5 Wh/l, frequently higher than or equal to 10 Wh/l and particularly higher than or equal to 15 Wh/l. That ratio is usually lower than or equal to 100 Wh/l, often lower than or equal to 75Wh/l, frequently lower than or equal to 50 Wh/l, and particularly lower than or equal to 40 Wh/l.

15 In that third variant, the concentration of "active chlorine" of the part of the reaction medium of step (a), preferably after acidification, is usually higher than or equal to 0.1 g of Cl₂/kg of the reaction medium of step (a), commonly higher than 0.2 g/kg and often higher than or equal to 0.3 g/kg. That concentration is usually lower than or equal to 100 g/kg, often lower than or equal to 10 g/kg, frequently lower than or equal to 1 g/kg, commonly lower than 0.8 g/kg and
20 often lower than or equal to 0.5 g/kg.

In that third variant, the pH of step (b2), at which the chloro-photolysis treatment is carried out is generally maintained at a value higher than or equal to 1, usually higher than or equal to 2, preferably higher than or equal to 3 and more preferably higher than or equal to 4. That pH is usually maintained at a value
25 lower than or equal to 6, preferably lower than or equal to 5 and more preferably lower than or equal to 4.5.

The chloro-photolysis treatment can be carried out in a discontinuous, continuous or semi-continuous mode. Those modes of operation are as defined above for the first embodiment.

30 The chloro-photolysis treatment can be carried out in one or more reaction zones. Those reaction zones are as defined above for the first embodiment.

In a fourth variant of the third embodiment, the chloro-photolysis treatment can also be carried out on the reaction medium after step (b2). This can be in a third step (c) consecutive to step (b2).

The chloro-photolysis treatment could also be carried out in place of step (a) or of step (b2). This embodiment would be useful when the content of the organic substances in the aqueous solution to be treated is low.

5 In these third and fourth variants, the conversion rate of the TOC content of the reaction medium after step (b2) is usually higher than or equal to 50 %, often higher than or equal to 70 %, frequently higher than or equal to 80 % and in particular higher than or equal to 90 %.

10 In these third and fourth variants, the TOC content of the reaction medium after step (b2) is usually lower than or equal to 30 mg C/l, preferably lower than or equal to 20 mg C/l, more preferably lower than or equal to 15 mg C/l and most preferably lower than or equal to 10 mg C/l. That TOC is usually higher than or equal to 0.1 mg C/kg.

15 In these third and fourth variants, the COD content of the reaction medium after step (b2) is usually lower than or equal to 250 mg O/kg, preferably lower than or equal to 150 mg O/kg and more preferably lower than or equal to 50 mg O/kg. That COD is usually higher than or equal to 1 mg O/kg.

20 In a fifth variant of that third embodiment, at least one additional compound selected the group consisting of chlorine, oxygenated chlorine compounds, and any mixture thereof is added to step (b2) and a treatment with UV-visible light is carried out during step (b2). The oxygenated chlorine compound can be selected from the group consisting of hypochlorite, chlorate, chlorine dioxide, dichlorine monoxide, and any mixture thereof.

The treatment with UV-visible light is as described for the third and fourth variants.

25 In that fifth variant, the concentration of "active chlorine" of the part of the reaction medium of step (a), preferably after acidification and after the additional compound addition, is usually higher than or equal to 0.1 g of Cl_2 /kg of aqueous composition, commonly higher than 0.2 g/kg and often higher than or equal to 0.3 g/kg. That concentration is generally lower than or equal to 100 g/kg, often lower than or equal to 10 g/kg, frequently lower than or equal to 1 g/kg of aqueous composition, commonly lower than 0.8 g/kg and often lower than or equal to 0.5 g/kg.

35 In a sixth variant of that third embodiment, at least one additional compound selected the group consisting of chlorine, oxygenated chlorine compounds, and any mixture thereof is added to step (b2) and a treatment with UV-visible light is carried out after step (b2). The oxygenated chlorine

compound can be selected from the group consisting of hypochlorite, chlorate, chlorine dioxide, dichlorine monoxide, and any mixture thereof. This can be in a third step (c) consecutive to step (b2).

5 The chloro-photolysis treatment could also be carried out in place of step (a) or of step (b2). This would however be useful when the content of the organic substances in the aqueous solution to be treated is low.

In a seventh variant of the third embodiment, during step (b2), a treatment by electrolysis is carried out on the reaction medium. This treatment will be referred hereafter as an electrolysis treatment.

10 The electrolysis treatment generally comprises passing a direct current through the reaction medium of step (b2) or applying a direct voltage across the reaction medium of step (b2). This treatment preferably comprises passing a direct current through the reaction medium of step (b2).

15 In the electrolysis treatment of the seventh variant, the temperature is often lower than or equal to 120°C, frequently lower than or equal to 100°C and particularly lower than or equal to 90°C. That temperature is usually higher than or equal to 0°C, often higher than or equal to 25°C, frequently higher than or equal to 50°C, particularly higher than or equal to 60°C and specifically higher than or equal to 70°C. A temperature of 85°C is particularly convenient.

20 In the electrolysis treatment of the seventh variant, the pressure is often lower than or equal to 5 bar absolute, frequently lower than or equal to 2 bar, particularly lower than or equal to 1.8 bar and specifically lower than or equal to 1.5 bar. That pressure is usually higher than or equal to 0.01 bar absolute, often higher than or equal to 0.1 bar, frequently higher than or equal to 0.5 bar, 25 particularly higher than or equal to 0.6 bar and specifically higher than or equal to 0.7 bar.

In the electrolysis treatment of the seventh variant, the pH of the part of the reaction medium of step (a), is generally maintained at a value higher than or equal to 2, often higher than or equal to 3 and frequently higher than or equal to 3.5. That pH is generally maintained at a value lower than or equal to 6, often 30 lower than or equal to 5 and frequently lower than or equal to 4.5.

That pH can be adjusted before or during the electrolysis treatment, by adding an acidic or a basic compound.

35 The electrolysis treatment can be carried out in a discontinuous, continuous or semi-continuous mode. Those modes of operation are as defined above for the first embodiment.

The electrolysis treatment can be carried out in one or more reaction zones. Those reaction zones are as defined above for the first embodiment.

5 In that seventh variant, when the electrolysis process is carried out in the discontinuous mode, the reaction time is generally lower than or equal to 10 h, often lower than or equal to 5 h, frequently lower than or equal to 2 h, particularly lower than or equal to 1 h and specifically lower than or equal to 0.5 h. That time is usually higher than or equal to 0.005 h, often higher than or equal to 0.05 h, frequently higher than or equal to 0.1 h, particularly higher than or equal to 0.15 h and specifically higher than or equal to 0.2 h.

10 In that seventh variant, when the electrolysis treatment is carried out in the continuous mode, the residence time is generally lower than or equal to 10 h, often lower than or equal to 5 h, frequently lower than or equal to 2 h, particularly lower than or equal to 1 h and specifically lower than or equal to 0.5 h. That residence time is usually higher than or equal to 0.005 h, often
15 higher than or equal to 0.5 h, frequently higher than or equal to 0.1 h, particularly higher than or equal to 0.15 h and specifically higher than or equal to 0.2 h. The residence time is defined as the ratio between the volume of the zone where the electrolysis treatment is carried out and the flow rate of the reaction medium fed to that zone.

20 The electrolysis process of the seventh variant is usually carried out in an electrolysis cell (or unit) comprising at least one anode and at least one cathode.

In the electrolysis treatment of the seventh variant, when the treatment is carried out under the direct current mode, the current density passed through the reaction medium is generally higher than or equal to 1 A/m^2 of electrode,
25 preferably of anode, often higher than or equal to 100 A/m^2 , frequently higher than or equal to 1000 A/m^2 and specifically higher than or equal to 5000 A/m^2 . That current density is generally lower than or equal to 25000 A/m^2 of electrode, preferably of anode, often lower than or equal to 20000 A/m^2 , frequently lower than or equal to 15000 A/m^2 and specifically lower than or equal to 10000 A/m^2 .

30 In the electrolysis treatment of the seventh variant, when the electrolysis is carried out under the direct voltage mode, the voltage applied between the anode and the cathode is generally higher than or equal to 2.3 V, often higher than or equal to 2.4 V and frequently higher than or equal to 2.5 V. That voltage is generally lower than or equal to 6 V, often lower than or equal to 5 V and
35 frequently lower than or equal to 4 V.

The electrolysis treatment of the seventh variant generally comprises applying a direct current or applying a direct voltage between the cathode and the anode, often comprises applying a direct current between the cathode and the anode.

5 The electrolysis cell can be a divided cell or an undivided cell. A divided cell is a cell where the anode and the cathode are separated, like in a mercury cell, a diaphragm cell, a membrane cell or a cell where the anodic compartment and cathodic compartments are linked by an electrolytic bridge. The electrolysis cell is often a divided cell. It is often a diaphragm cell or a membrane cell, and
10 frequently a membrane cell. A mercury cell is also convenient. The advantage of using a divided cell is to avoid the contact between the products formed at the anode and the products formed at the cathode.

When the electrolysis cell is a diaphragm or a membrane cell, it generally comprises an anolyte compartment containing at least one anode and a catholyte
15 compartment containing at least one cathode, the compartments being separated by a least one diaphragm or at least one membrane. The part of the reaction medium of step (a) to be submitted to the electrolysis treatment can be fed to the anolyte compartment, to the catholyte compartment or to both compartments of the electrolysis cell. It is preferably fed to the anolyte compartment.

20 The ratio between the surface of the electrode, preferably the anode, and the volume of the reaction medium of step (b2) is usually higher than or equal to 0.001 cm^{-1} , often higher than or equal to 0.005 cm^{-1} , frequently higher than or equal to 0.01 cm^{-1} , in many cases higher than or equal to 0.1 cm^{-1} , and in particular higher than or equal to 0.2 cm^{-1} . That surface to volume ratio is
25 usually lower than or equal to 1 cm^{-1} , often lower than or equal to 0.5 cm^{-1} , frequently lower than or equal to 0.4 cm^{-1} and in particular higher than or equal to 0.3 cm^{-1} . When an undivided electrolysis cell is used, the volume of the reaction medium of step (b2) is the volume of that medium in the electrolysis cell. When a divided electrolysis cell is used, the volume of the reaction medium
30 of step (b2) is the volume of that medium in the anodic compartment or in the cathodic compartment of the electrolysis cell, preferably in the anodic compartment.

35 The characteristics of the various type of electrolysis cells, of the anodes and cathodes, of the membranes and diaphragms, etc. can be found in Ullmann's Encyclopedia of Industrial Chemistry, Fifth Completely Revised Edition, Vol. A6 1986, pp. 401-477.

In the seventh variant of the third embodiment, the conversion rate of the TOC content of the reaction medium after step (b2) is usually higher than or equal to 25 %, often higher than or equal to 30 %, frequently higher than or equal to 50 % and in particular higher than or equal to 70 %.

5 In an eight variant of the third embodiment, the electrolysis treatment can also be carried out on the reaction medium after step (b2). This can be in a third step (c''') consecutive to step (b2).

10 In a ninth variant of the third embodiment, at least one additional compound selected from the group consisting of chlorine, oxygenated chlorine compounds, and any mixture thereof is added to step (b2) and during step (b2) and a treatment by electrolysis is carried out. The oxygenated chlorine compound can be selected from the group consisting of hypochlorite, chlorate, chlorine dioxide, dichlorine monoxide, and any mixture thereof.

15 In a tenth variant of the third embodiment, at least one additional compound selected from the group consisting of chlorine, oxygenated chlorine compounds, and any mixture thereof is added to step (b2) and after step (b2) and a treatment by electrolysis is carried out. The oxygenated chlorine compound can be selected from the group consisting of hypochlorite, chlorate, chlorine dioxide, dichlorine monoxide, and any mixture thereof.

20 The treatment by electrolysis of the ninth and tenth variants are as described in the seventh variant of the third embodiment.

The electrolysis treatment could also be carried out in place of step (a) or of step (b2). This embodiment would be useful when the content of the organic substances in the aqueous solution to be treated is low.

25 In an eleventh variant of the third embodiment, during step (b2), a treatment with UV-visible light and an electrolysis treatment are carried out.

In a twelfth variant of the third embodiment, after step (b2), a treatment with UV-visible light and an electrolysis treatment are carried out.

30 In a first aspect of this twelfth variant, the two treatments are carried out simultaneously, after step (b2).

In a second aspect of this twelfth variant, the two treatments are carried out sequentially, after step (b2). Any sequence is convenient.

35 In a thirteenth variant of the third embodiment, during step (b2), a treatment with UV-visible light is carried out and, after step (b2) an electrolysis treatment is carried out.

In a fourteenth variant of the third embodiment, during step (b2), an electrolysis treatment is carried out and after step (b2), a treatment with UV-visible light is carried out.

5 In further fifteenth to eighteenth variants, of the third embodiment, at least one additional compound selected from the group consisting of chlorine, oxygenated chlorine compounds, and any mixture thereof is added to step (b2) and the UV and electrolysis treatments of the variants 11 to 14 are carried out. The oxygenated chlorine compound can be selected from the group consisting of hypochlorite, chlorate, chlorine dioxide, dichlorine monoxide, and any mixture
10 thereof.

The UV-visible and electrolysis treatments of those eleventh to fourteenth variants are as described above, respectively for the third and seventh variants.

15 In a nineteenth variant of the third embodiment, at least one part of the reaction medium of step (b2) is subjected to an operation selected from the group consisting of cooling, evaporative crystallization, and any combination thereof, in order to recover at least one salt that might be present in the reaction medium of step (b2) and at least one aqueous composition. In that variant, step (b1) is carried out on the reaction medium obtained at the end of step (b2).

20 In the process according to the invention, usually, at least one of the steps (a), (b1) and (b2) is carried out in a continuous mode. Preferably, all of the steps (a), (b1) and (b2) are carried out in a continuous mode.

The various variants of the second embodiment of the process according to the invention can be envisioned as various aspects of the nineteenth variant of the third embodiment of the process according to the invention.

25 Any combination between at least two variants of the third embodiment can be envisioned.

30 In the process for degrading the organic substances of the aqueous composition according to the invention the various steps are preferably carried out in equipment produced from or covered with materials that are resistant to the treatment conditions. Those materials are such as described in the International application WO 2008/152043 of SOLVAY SA, the content of which is incorporated herein by reference, more specifically the passage from page 29, line 20 to page 30, line 20.

35 The reaction medium obtained after the treatments of the first and third embodiments, the salt recovered in the second embodiment and the solution obtained by combining the salt and the evaporate recovered in the second variant

of the second embodiment can be used as a starting material in an electrolysis process, preferably in an electrolysis process for producing chlorine, preferably an electrolysis process for industrially producing chlorine, and more preferably for an electrolysis process for industrially producing chlorine from brine, as disclosed in the International application WO 2008/152043 of SOLVAY SA, the content of which is incorporated herein by reference, more specifically the passage from page 31, line 2 to page 35, line 2. The reaction medium can be submitted to classical treatment before being used in such electrolysis processes like for instance dechlorination, NaCl saturation or ion-exchange resin treatments.

The transfer of the reaction medium obtained after the treatments of the first and third embodiments and of the solution obtained in the second variant of the second embodiment to the electrolysis process is usually carried in equipment produced from or covered with materials that do not release components which could be detrimental to the electrolysis process.

By way of suitable material, mention may be made, for example, of enamelled steel, polymers like, polyolefins such as polypropylene and polyethylene, chlorinated polymers such as polyvinyl chloride and chlorinated polyvinyl chloride, fluorinated polymers such as totally fluorinated polymers like, polytetrafluoroethylene, copolymers of tetrafluoroethylene and hexafluoropropylene, and poly(perfluoropropylvinylether), such as partially fluorinated polymers like poly(vinylidene fluoride), copolymers of ethylene and chlorotrifluoroethylene, polymers comprising sulphur, such as polysulphones or polysulphides, in particular aromatic, coatings by means of resins among which, epoxy resins or phenolic resins, metals such as tantalum, titanium, copper, gold and silver, nickel and molybdenum, or alloys thereof, more particularly alloys containing nickel and molybdenum.

Polyolefins, in particular polypropylene are particularly convenient when the reaction medium does not contain any remaining "active chlorine", *i.e.*, the "active chlorine" content is lower than or equal to 1 mg of Cl_2/kg , preferably lower than or equal to 0.5 mg of Cl_2/kg and more preferably lower than or equal to 0.1 mg of Cl_2/kg .

When the reaction medium still contains remaining "active chlorine", *i.e.*, the "active chlorine content is higher than 1 mg of Cl_2/kg , preferably higher than or equal to 10 mg of Cl_2/kg and more preferably higher than or equal to 100 mg

of Cl_2/kg , it is preferred to use chlorinated polymers, fluorinated polymers, metals or alloys.

Polyvinyl chloride, polyvinylidene fluoride, and copolymers of ethylene and chlorotrifluoroethylene are particularly suitable when the pH of the reaction medium or of the solution is lower than or equal to 5, preferably lower than or equal to 4 and more preferably lower than or equal to 3.

Perfluorinated polymers such as polytetrafluoroethylene, copolymers of tetrafluoroethylene and hexafluoropropylene, and poly(perfluoropropylvinylether) can be used in the presence of active chlorine at any pH but they are particularly convenient when the pH of the reaction medium or of the solution is higher than 5, preferably higher than or equal to 7 and more preferably higher than or equal to 9.

Metals like tantalum and titanium, alloys like Hastelloy C, and enamelled steel can be used in the presence of active chlorine at any pH but they are particularly convenient when the pH of the reaction medium or of the solution is higher than 5, preferably higher than or equal to 7 and more preferably higher than or equal to 9.

In the variants of the third embodiment where an electrolysis treatment is carried out, the electrolysis treatment can be carried out in an electrolysis cell for producing chlorine. This has the advantage of combining the production of chlorine and the degradation of the organic compounds present in the aqueous composition to be treated. The degradation of the organic compounds during the electrolysis for producing chlorine has the following advantages. Firstly, it can reduce the TOC in the depleted brine to be recycled to the electrolysis cell. Secondly, it can concomitantly reduce the frequency of the purge of the recycled brine and the TOC of that purge. These advantages leads to a reduction in the number process steps, with a favorable economic impact.

Example 1

A glass thermostated jacketed reactor having a working volume of 1 l and fitted with a vertical condenser has been supplied with 269 g of a brine containing per kg, 4.76 g of 3-chloropropane-1,2-diol, 5.03 g of 1,3-dichloro-2-propanol, 2.39 g of 2,3-dichloro-1-propanol, 0.17 g of glycerol (1,2,3-propanetriol), 217 g of sodium chloride, the balance being water. The TOC of that brine was 4.2 g C/l and the calculated COD was 11.5 g O/kg. That brine has been heated at reflux ($\sim 107^\circ\text{C}$) under atmospheric pressure (~ 1013 mbar absolute) and under stirring (magnetic bar). To the heated brine, a

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first fraction (63.2 g) of an aqueous hypochlorite solution containing per kg, 1.532 mol of sodium hypochlorite (NaOCl), 0.006 mol of sodium chlorate (NaClO₃), 0.100 mol of sodium hydroxide, 1.54 mol of sodium chloride, the balance being demineralized water has been added at once (time zero). A
 5 second, a third and a fourth fraction (respectively of 62.7 g, 63.8 g and 63.5 g) have been added, each at once, after respectively 15, 30 and 45 minutes.

The pH of the resulting mixtures has been maintained at a value of 8 (+/- 0.1) at 106°C (8.5 +/- 0.1 at 25°C) by regular addition of a sodium hydroxide solution (1 M) during the first 20 minutes (45 ml of NaOH 1 M
 10 added), and by regular addition of a hydrogen chloride solution (1 M) after the first 20 minutes. After 45 min, samples have been regularly withdrawn from the reaction mixture for analysis.

The samples have been analyzed by iodometry (ClO⁻ and ClO₃⁻) and mercurimetry (Cl⁻). The samples have been treated with an excess of sodium
 15 sulfite and then analyzed for their TOC content according to the methods mentioned above.

The results have been summarized in Table 1.

Table 1

Ex.	ClO ⁻ /COD (gCl ₂ /gCl ₂)	Time (min)	pH	ClO ₃ ⁻ (mmol/kg)	TOC (mgC/l)	TOC conv (%)
1	2.0	45	8.43	49	63	97.1
		75	8.00	88	18	99.2
		105	8.00	90	12	99.4
		135	8.00	90	11	99.5
		165	7.99	92	11	99.5
		285	7.97	83	11	99.5

The quantity of ClO⁻ and the COD have been expressed in g Cl₂ according
 20 to the following rules : 1 g ClO⁻ corresponds to 1.38 g Cl₂, and 1 g O corresponds to 4.43 g of Cl₂.

Examples 2 and 3

The procedure of example 1 has been followed except that the amount of the hypochlorite added and the pH have been modified as described in Table 2.

Table 2

Ex.	ClO ⁻ /COD (gCl ₂ /gCl ₂)	Time (min)	pH	ClO ₃ ⁻ (mmol/kg)	TOC (mgC/l)	TOC conv (%)
1	2.0	165	7.99	92	11	99.5
2	2.0	165	8.1	101.5	7	99.7
3	1.57	165	7.99	48.8	15	99.4

Examples 4 to 7

The procedure of example 1 has been followed except that the brine to be treated did not contain any monochloropropanediol, that the amount of the hypochlorite added and the pH have been modified as described in Table 3, where the results have also been summarized.

Table 3

Ex.	ClO-/COD (gCl ₂ /gCl ₂)	Time (min)	pH	ClO ₃ - (mmol/kg)	TOC (mgC/l)	TOC conv (%)
4	2.7	165	9.30	13	16	95.9
5	2.8	165	8.1	27.7	< 5	> 97
6	2.0	165	12.2	6.9	120	69.6
7	2.0	165	8.8	13	< 5	> 97

Example 8

A first glass thermostated jacketed reactor (R1) having a working volume of 400 ml, fitted with a vertical refrigerant and a magnetic bar, has been supplied continuously with :

- a brine containing per kg, 1.989 g of ethylene glycol, 3.580 g of formic acid, 16.53 g of sodium chloride, the balance being water. The calculated TOC of that brine was 1.70 g C/l and the calculated COD was 3.81 g O/kg (16.91 g Cl₂/kg).
- a first stream of an aqueous hypochlorite solution containing per kg, 1.550 mol of sodium hypochlorite (NaOCl, 109.92 g Cl₂/kg), 0.0123 mol of sodium chlorate (NaClO₃), 0.133 mol of sodium hydroxide, 1.708 mol of sodium chloride, the balance being demineralized water.

A second glass thermostated jacketed reactor (R2) having a working volume of 400 ml, fitted with a vertical refrigerant and a magnetic bar, has been supplied continuously with :

- the liquid mixture exiting the first reactor by continuous overflow
- a second stream of the aqueous hypochlorite solution.

A third glass thermostated jacketed reactor (R3) having a working volume of 307 ml and fitted with a vertical refrigerant has been supplied continuously with :

- the liquid mixture exiting the second reactor by continuous overflow.

The reaction medium in the first and second reactor have been heated at reflux (~ 105°C) under atmospheric pressure (~ 1013 mbar absolute) and under stirring (magnetic bar). The reaction medium in the third reactor has been heated to a temperature just below its boiling point under atmospheric pressure with no

stirring. The first two reactor simulate perfectly stirred tanks reactors while the third one simulate a plug-flow reactor.

The pH of the reaction medium in the first two reactors is regulated by addition of a 37 % hydrogen chloride aqueous solution.

5 The top of the vertical refrigerants has continuously been flushed with nitrogen, and the flushed gas has been trapped in a scrubber containing an aqueous solution of NaOH 3M.

10 The samples have been analyzed by iodometry (ClO^- and ClO_3^-) and mercurimetry (Cl^-). The samples have been treated with an excess of sodium sulfite and then analyzed for their TOC content according to the methods mentioned above. Carboxylic acids have been measured by ionic chromatography and aldehydes have been measured by high performance liquid chromatography (HPLC) after derivatization into hydrazone. The flushed gas have been analyzed by gas chromatography and the scrubber content has been
15 analyzed for hypochlorite by iodometry and for weak bases by acidimetry.

The results have been summarized in Table 4.

Examples 9 and 10

20 The procedure of example 8 has been followed except that the hypochlorite solution contained per kg, 1.327 mol of sodium hypochlorite (NaOCl , 94.10 g Cl_2/kg), 0.0037 mol of sodium chlorate (NaClO_3), 0.58 mol of sodium hydroxide, 1.914 mol of sodium chloride, the balance being demineralized water.

The results have been summarized in Table 4.

Table 4

Ex.	Brine) (ml/h)	ClO ⁻ (ml/h)	ClO ⁻ (ml/h)	Residence time (min)			pH (25°C)			ClO ₃ ⁻ (mmol/kg)	TOC (mgC/l)	TOC Conv (%)
	(R1)	(R1)	(R2)	(R1)	(R2)	(R3)	(R1)	(R2)	(R3)			
8	1080	182	91	16.4	14.7	12.5	6.2	6.1	6.1	40.2	8	99.4
9	1080	212	106	16.9	14.9	12.6	8.9	9.5	9.0	7.8	210	83.5
10	1080	212	106	16.5	13.8	11.7	8.5	8.8	8.3	29	110	90.7

Example 11

The treatment has been carried out in a glass thermostated reactor equipped with a magnetic stirring bar coated with polytetrafluoroethylene, a thermocouple sensor in a glass jacket, a pH electrode, a tube for chlorine gas addition and a vertical condenser connected to a scrubber.

581.6 g of a 20 % by weight NaCl aqueous solution containing 989 mg/l of acetic acid and 493 mg/l of propionic acid have been added to the reactor. The TOC content was 635 mg C/l. This solution simulates a reaction medium obtained after the treatment of step (a) according to the first embodiment of the invention.

A continuous injection of chlorine gas in the solution has been carried out at 80°C, in order to maintain the gas saturation of the solution. The total pressure was of 1 bar. The chlorine partial pressure has been estimated to 0.6 bar as the water vapor pressure above the solution is 0.4 bar at 80°C. The pH value of the solution saturated with chlorine (measured at room temperature) has been adjusted and maintained between 3.95 and 4.56 by addition of pellets of caustic soda in the saturated solution during the introduction of chlorine. The results of the treatment are summarized in Table 5. The time zero has been taken as the time of starting the injection of chlorine in the solution.

Table 5

Time (min)	TOC (mg C/l)	Acetic acid (mg/l)	Propionic acid (mg/l)	Bromide (mg/l)	Chlorate (mg/l)	Total caustic soda added (mg)
15	617	940	410	6.3	29	694
30	605	870	380	7.1	18	1082
45	582	840	350	13	43	1082
60	560	810	310	15	52	1322
90	522	750	260	15	85	1322
120	482	690	210	17	120	1322

Example 12

The equipment and the procedure of example 11 have been used.

603.7 g of a 20 % by weight NaCl aqueous solution containing 1021 mg/l of acetic acid and 509 mg/l of propionic acid have been used. The TOC content was 656 mg C/l. This solution simulates a reaction medium obtained after the treatment of step (a) according to the first embodiment of the invention.

The temperature of the treatment was 100°C and the total pressure was 1 bar. The chlorine partial pressure has been estimated to 0.15 bar as the water vapor pressure above the solution is 0.85 bar at this temperature. The pH has been adjusted and maintained between 3.8 and 4.5 by addition of pellets of caustic soda in the saturated solution during the injection of chlorine. The results are summarized in Table 6. The time zero has been taken as the time of starting the injection of chlorine in the solution.

Table 6

Time (min)	TOC (mg C/l)	Acetic acid (mg/l)	Propionic acid (mg/l)	Chlorate (mg/l)	Total caustic soda added (mg)
15	654	990	430	< 1	251
30	602	900	340	11	412
45	526	780	260	14	412
60	479	710	190	17	651

Example 13

The procedure of example 8 has been followed.

The brine engaged in the treatment contained per kg, 0.69 g of glycerol, 0.59 g of 1-chloro-2,3-propanediol, 0.08 g of 2-chloro-1,3-propanediol, 0.39 g of epichlorohydrin, 0.08 g of hydroxyacetone, 0.073 g of acetic acid, 0.050 g of formic acid, 0.018 g of lactic acid, 0.012 g of propionic acid and 16.53 g of sodium chloride. The sodium chloride content of the brine was 176 g/l and the balance was water. The measured TOC of that brine was 1.4 g C/l and the measured COD was 3.9 g O/l.

The hypochlorite solution contained per kg, 1.39 mol of sodium hypochlorite (NaOCl , 98.7 g Cl_2/kg), 0.010 mol of sodium chlorate (NaClO_3), 0.55 mol of sodium hydroxide, 1.45 mol of sodium chloride, the balance being demineralized water.

The pH of the reaction medium in the first two reactors has been regulated by addition of a 6 % hydrogen chloride aqueous solution.

A brine with a TOC value of 0.085 g C/l has been recovered at the output of the third reactor. That brine contained per kg, 2.65 mol of NaCl , 0.016 mol of sodium hypochlorite, 0.033 mol of sodium chlorate, 0.12 g of acetic acid, 0.012 g of propionic acid, 0.008 g of formic acid, 0.005 g of lactic acid, 0.006 g of succinic acid and 0.003 g of adipic acid.

A sample of 1873 g of this brine has been transferred in a thermostated glass reactor equipped with a magnetic stirring rod covered with

polytetrafluoroethylene, a pH electrode, a thermocouple sensor in a glass jacket, a medium UV lamp in a quartz jacket and a vertical condenser connected to a scrubber. The UV lamp was a HERAEUS UV immersion lamp TQ150 with an input rating of 150W. The brine has been heated at 80°C under stirring and the pH has been adjusted at 4.4 by addition of 55 ml of HCl 6N. The irradiation has then been started. The TOC value has decreased to 0.013 g/l and 0.009 g/l after respectively 20 min and 35 min of irradiation time. The brine contained finally per kg, 0.008 g of acetic acid, 0.006 g of lactic acid and 0.003 g of formic acid.

Example 14

A glass reactor of 5 l fitted with a magnetic bar for stirring, a Medium pressure High Tech QC lamp from Heraeus-Noblelight with an input rating of 150W in a centrally positioned quartz jacket, a vertical condenser connected to a scrubber, means for introducing liquids and an overflow system has been used.

The reactor has been fed with an aqueous solution containing 0.74 g/kg of active chlorine, 3.06 g/kg of sodium chlorate, 170 g/kg of sodium chloride, 0.162 g/l of acetic acid, 0.020 g/l of glycolic acid, 0.018 g/l of formic acid, 0.015 g/l of lactic acid and 0.005 g/l of propionic acid (TOC content of 0.092 g C/l) at a rate of 5 l/h and with an aqueous solution of sodium hypochlorite at the concentration of 2.03 mol/kg at a rate of 50 ml/h.

The aqueous solution was a reaction medium obtained after the treatment of step (a) according to the first embodiment of the invention.

The pH has been regulated at 4.2 with the addition of HCl 37 % by weight. The temperature has been set between 80 and 85°C. The total pressure was 1 bar. The residence time of the liquid in the reactor was 60 min. The lamp has been operated at an energy dissipation of 30 Wh/l. The brine collected at the output of the photoreactor contained 0.05 g/kg of active chlorine, 4.35 g/kg of sodium chlorate, 0.009 g/l of acetic acid and 0.001 g/l of formic acid. The TOC content was 0.015 g C/l.

Example 15

The conditions of example 14 have been used excepted that the brine flow rate has been increased to 10 l/h, so that the energy dissipation of the lamp has been of 15 Wh/l. The brine before the treatment contained 3.36 g/kg of active chlorine, 3.86 g/kg of sodium chlorate, 170 g/kg of sodium chloride, 0.145 g/l of acetic acid, 0.023 g/l of glycolic acid and 0.035 g/l of formic acid (TOC content of 0.066 g C/l). No additional active chlorine has been added to the reactor and

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the pH has been regulated at 4.2 with the addition of HCl 37 % by weight. The temperature has been set at 95°C. The residence time of the liquid in the reactor was 30 min. The brine collected at the output of the reactor contained 0.55 g/kg of active chlorine, 4.3 g/kg of sodium chlorate, 0.042 g/l of acetic acid. The TOC content was 0.024 g C/l.

Example 16

An undivided electrolysis cell of 1 liter, comprising an anode and a cathode and a stirring device has been used. The anode consisted of a Titanium substrate on which an electrochemical coating has been applied. The test has been carried out under discontinuous mode. The cell has been filled with an aqueous composition comprising per kg of composition, 163 g of sodium chloride, and per liter of composition 135 mg of acetic acid, 46 mg of glycolic acid and 2 mg of formic acid, and a TOC of 130 mg of C/l.

The aqueous solution was a reaction medium obtained after the treatment of step (a) according to the first embodiment of the invention.

A direct current density of 1 kA per m² has been applied at the anode. The temperature of cell has been maintained at 75°C and at a total pressure at 1 bar absolute. The ratio between the anode surface and the volume of the aqueous composition was 0.01 cm⁻¹. The pH has been kept at 4.5 during the electrolysis.

The TOC conversion has been recorded as a function of the electrical charge passed. The results are presented in Table 7.

Example 17

The conditions of example 16 have been used except that the ratio between the anode surface and the volume of the aqueous composition was 0.28 cm⁻¹.

The results are presented in Table 7.

Example 18

The conditions of example 16 have been used except that the direct current density was 0.1 kA/m². The results are presented in Table 7.

Table 7

Charge (Ah/m ²)	TOC conversion (%)		
	Example 16	Example 17	Example 18
50	n.m.	27	49
83	35	n.m.	n.m.
100	n.m.	43	54
167	45	n.m.	n.m.
333	n.m.	50	n.m.
500	53	n.m.	n.m.
1000	78	68	n.m.

n.m. : not measured

Example 19

The conditions of example 16 have been used except that the ratio between the anode surface and the volume of the aqueous composition was 0.28 cm⁻¹. The acetic acid conversion has been recorded as a function of the electrical charge passed. The results are presented in Table 8.

Example 20

The conditions of example 19 have been used except that direct current density of 0.5 kA per m² of electrode. The results are presented in Table 8.

Example 21

The conditions of example 19 have been used except that the direct current density was 0.1 kA/m². The results are presented in Table 8.

Table 8

Charge (Ah/m ²)	Acetic acid conversion (%)		
	Example 19	Example 20	Example 21
50	1	2	8
100	2	n.m.	12
333	11	6	n.m.
1000	11	n.m.	n.m.

n.m. : not measured

Example 22

An electrolysis cell of 0.6 liter, comprising an anolyte compartment with one anode and a catholyte compartment with one cathode, separated by a membrane, has been used. The anode consisted of a Titanium substrate on which an electrochemical coating has been applied. The cathode consisted of a nickel substrate on which an electrochemical coating has been applied. The membrane was an Asahi Glass Company – Flemion F8020 membrane. The

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NaOH concentration in the catholyte compartment has been set to 32 % by weight of NaOH by continuously feeding the catholyte compartment with an aqueous composition containing 29 % by weight of NaOH. The NaCl concentration in the anolyte compartment has been set to 19 % by weight by continuously feeding the anolyte compartment with an aqueous composition comprising per kg of composition, 250 g of sodium chloride, and per liter of composition 120 mg of acetic acid, 21 mg of dichloroacetic acid, 20 mg of glycerol, 1.5 mg of succinic acid, 1.5 mg of oxalic acid, 1 mg of glyceraldehyde, 0.5 mg of formaldehyde, and a TOC of 70 mg of C/l.

The aqueous solution was a reaction medium obtained after the treatment of step (a) according to the first embodiment of the invention. The solution has been submitted to typical dechlorination, NaCl saturation and ion-exchange resin treatments before being fed to the cell.

A direct current density of 4 kA per m² of electrode has been applied between the anode and the cathode. The temperature of cell has been maintained at 85°C and at a total pressure at 1 bar absolute.

The TOC value in the brine at the outlet of the anolyte compartment of the cell was 58 mg of C/l.

The TOC conversion in the brine at the outlet of the anolyte compartment of the cell was 34 %.

Example 23

The conditions of example 22 have been used except that the anolyte compartment has been fed with an aqueous composition comprising per kg of composition, 250 g of sodium chloride, and per liter of composition 130 mg of acetic acid, 32 mg of dichloroacetic acid, 22 mg of glycerol, 12 mg of propionic acid, 3.1 mg of succinic acid, 2.7 mg of oxalic acid, 0.3 mg of glyceraldehyde, 0.6 mg of formaldehyde, and a TOC of 85 mg of C/l.

The aqueous solution was a reaction medium obtained after the treatment of step (a) according to the first embodiment of the invention. The solution has been submitted to typical dechlorination, NaCl saturation and ion-exchange resin treatments before being fed to the cell.

The TOC value in the brine at the outlet of the anolyte compartment of the cell was 75 mg of C/l.

The TOC conversion in the brine at the outlet of the anolyte compartment of the cell was 31 %.

Example 24

The conditions of example 22 have been used except that the anolyte compartment has been fed with an aqueous composition comprising per kg of composition, 250 g of sodium chloride, and per liter of composition 70 mg of acetic acid, 25 mg of formic acid, 10 mg of oxalic acid and 5 mg of dichloroacetic acid, and a TOC of 65 mg of C/l.

The aqueous solution was a reaction medium obtained after the treatment of step (a) according to the first embodiment of the invention. The solution has been submitted to typical dechlorination, NaCl saturation and ion-exchange resin treatments before being fed to the cell.

The TOC value in the brine at the outlet of the anolyte compartment of the cell was 24 mg of C/l.

The TOC conversion in the brine at the outlet of the anolyte compartment of the cell was 68 %.

Example 25

The procedure of example 8 has been followed.

The brine engaged in the treatment contained per kg, 0.69 g of glycerol, 0.59 g of 1-chloro-2,3-propanediol, 0.08 g of 2-chloro-1,3-propanediol, 0.39 g of epichlorohydrin, 0.08 g of hydroxyacetone, 0.073 g of acetic acid, 0.050 g of formic acid, 0.018 g of lactic acid, 0.012 g of propionic acid and 16.53 g of sodium chloride. The sodium chloride content of the brine was 176 g/l and the balance was water. The measured TOC of that brine was 1.4 g C/l and the measured COD was 3.9 g O/l.

The hypochlorite solution contained per kg, 1.39 mol of sodium hypochlorite (NaOCl , 98.7 g Cl_2/kg), 0.010 mol of sodium chlorate (NaClO_3), 0.55 mol of sodium hydroxide, 1.45 mol of sodium chloride, the balance being demineralized water.

The pH of the reaction medium in the first two reactors has been regulated by addition of a 6 % hydrogen chloride aqueous solution.

A brine with a TOC value of 0.085 g C/l has been recovered at the output of the third reactor. That brine contained per kg, 2.65 mol of NaCl, 0.016 mol of sodium hypochlorite, 0.033 mol of sodium chlorate, 0.12 g of acetic acid, 0.012 g of propionic acid, 0.008 g of formic acid, 0.005 g of lactic acid, 0.006 g of succinic acid and 0.003 g of adipic acid. The pH of the brine was 7.1.

The brine has been acidified to pH 1.6 by addition of concentrated hydrochloric acid and chlorine was stripped by flushing nitrogen. After that, pellets of caustic soda have been added to set the pH of the brine at 7.6.

5 A sample of 505.8 g of that brine has been submitted to evaporative crystallization treatment by heating to boil at normal pressure in a 1 liter glass flask equipped with a polytetrafluoroethylene coated magnetic rod, with a thermocouple sensor in a glass jacket and with a head of distillation connected to a condenser cooled with water at 25°C.

10 257.7 g of a first water evaporate have been collected and a first residue of evaporation has been obtained. A first fraction of crystallized sodium chloride has been recovered by filtration of the first residue of evaporation and washed with 18 g of demineralized water. The first wet salt recovered after washing weighted 21.9 g. The first filtrate weighted 217.1 g.

15 195.1 g of the first filtrate have been submitted to evaporation in the same equipment.

106.1 g of a second water evaporate have been collected and a second residue of evaporation has been obtained.

20 A second fraction of crystallized sodium chloride has been recovered by filtration of the second residue of evaporation and washed with 25 g of demineralized water. The second wet salt recovered after washing weighted 41.33 g. The second filtrate weighted 32.46 g.

25 The TOC values have been determined for all the distillates and filtrates as such and for the wet sodium chloride fractions after dissolution of the salt in water so as to obtain a 20 % by weight of salt solution. The results are summarized in the Table 9.

Example 26

The brine used in the example 25 has been submitted to the evaporative crystallization treatment of example 25 directly *i.e.* without applying the hypochlorite treatment.

30 A sample of 508.7 g of that brine has been submitted to evaporative crystallization treatment by heating to boil at normal pressure in a 1 liter glass flask equipped with a polytetrafluoroethylene coated magnetic rod, with a thermocouple sensor in a glass jacket and with a head of distillation connected to a condenser cooled with water at 25°C.

35 249 g of a first water evaporate have been collected and a first residue of evaporation has been obtained. A first fraction of crystallized sodium chloride

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has been recovered by filtration of the first residue of evaporation and washed with 12.2 g of demineralized water. The first wet salt recovered after washing weighted 15.95 g. The first filtrate weighted 250.1 g.

5 208.8 g of the first filtrate have been submitted to evaporation in the same equipment.

102.7 g of a second water evaporate have been collected and a second residue of evaporation has been obtained.

A second fraction of crystallized sodium chloride has been recovered by filtration of the second residue of evaporation and washed with 11.5 g of demineralized water. The second wet salt recovered after washing weighted 47.23 g. The second filtrate weighted 50.6 g.

The TOC values have been determined for all the distillates and filtrates as such and for the wet sodium chloride fractions after dissolution of the salt in water so as to obtain a 20 % by weight of salt solution. The results are summarized in Table 9.

Table 9

Example	First Filtrate (mgC/l)	Second Filtrate (mgC/l)	First Distillate (mgC/l)	Second Distillate (mgC/l)	First Wet Salt (mgC/l)	Second Wet Salt (mgC/l)
25	181	685	1.6	1.9	3	4
26	2900	8000	85	110	15	220

CLAIMS

1. Process for degrading organic substances in an aqueous composition comprising a step (a) wherein, in a liquid reaction medium, said aqueous composition is reacted with at least one composition comprising hydroxide ions (OH^-) and hypochlorite in a molar ratio between hydroxide and hypochlorite higher than or equal to 0.001 and lower than 1.5, in order to oxidize said organic substances.
2. Process according to claim 1 wherein the aqueous composition containing the organic substances contains at least one salt, comprising a further step (b1), wherein at least part of the reaction medium of step (a) is subjected to an operation selected from the group consisting of cooling, evaporative crystallization, and any combination thereof, in order to precipitate at least part of the salt, followed by a step wherein at least part of the precipitated salt and at least part of the water present in the aqueous composition are recovered.
3. Process according to claim 1 or 2 wherein step (a) is carried out at a first pH value and comprising a further step (b2), wherein, at least part of the reaction medium of step (a) is subjected to an acidification operation in order to bring the pH at a second value lower than the first pH value of step (a) and the organic substances are further oxidized.
4. Process according to claim 3, wherein at least one compound selected from the group consisting of chlorine, hypochlorite, chlorate, chlorine dioxide, dichlorine monoxide, and any mixture thereof, is added to the reaction medium of step (b2).
5. Process according to claim 4, wherein the compound is chlorine and the partial pressure of chlorine during step (b2) is higher than or equal to 0.001 bar and lower than or equal to 10 bar.
6. Process according to any of claims 3 to 5, wherein during or after step (b2), a treatment with UV-visible light is carried out on the reaction medium.

7. Process according to claim 6, wherein the UV-visible light has a wavelength higher than or equal to 100 nm and lower than or equal to 400 nm, wherein the UV-visible light is emitted by a source and wherein the ratio between the electrical energy consumed by the source in Wh and the volume of the treated part of the reaction medium of step (a) in liter is higher than or equal to 1 Wh/l and lower than or equal to 100 Wh/l.

8. Process according to any of claims 3 to 7, wherein during or after step (b2), a treatment by electrolysis is carried out on the reaction medium.

9. Process according to claim 8, wherein the treatment by electrolysis is carried out in an anodic compartment of a divided electrolysis cell, wherein the anodic current density is higher than or equal to 1 A/m² of anode and lower than or equal to 25000 A/m² of anode and wherein the ratio between the surface of the anode and the volume of the part of the treated reaction medium from step (a) is higher than or equal to 0.001 cm⁻¹ and lower than or equal to 1 cm⁻¹.

10. Process according to any of claims 3 to 9, wherein step (b1) is carried out on the reaction medium obtained at the end of step (b2).

11. Process according to any of claims 2 to 10 wherein at least one of the steps (a), (b1) and (b2) is carried out in a continuous mode.

12. Process according to any of claims 1 to 11 wherein the reaction of step (a) is carried out in at least one of the following conditions :

- i. a pH controlled and maintained in a range which lowest limit is higher than or equal to 6 and which highest limit is lower than or equal to 11,
- ii. a temperature higher than or equal to 10°C and lower than or equal to 200°C,
- iii. a pressure higher than or equal to 1 bar (absolute) and lower than or equal to 11 bar,
- iv. when step (a) of the process is carried out in a discontinuous mode, a duration higher than or equal to 0.05 h and lower than or equal to 8 h,
- v. when step (a) of the process is carried out in a continuous mode, a residence time higher than or equal to 0.05 h and lower than or equal to 8 h.

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13. Process according to any of claims 1 to 10 wherein step (a) is carried out in a continuous mode, and wherein the reaction of step (a) is carried out in at least two consecutive reaction zones, at least one of which is operated under mixed regime and at least one other of which is operated under plug flow regime.

5 14. Process according to any of claims 3 to 13 wherein the reaction of step (b2) is carried out in at least one of the following conditions :

- i. a pH controlled and maintained in a range which lowest limit is higher than or equal to 0.01 and which highest limit is lower than 6,
- ii. a temperature higher than or equal to 10°C and lower than or equal to 200°C,
- 10 iii. a pressure higher than or equal to 1 bar (absolute) and lower than or equal to 11 bar,
- iv. when step (b2) of the process is carried out in a discontinuous mode, a duration higher than or equal to 0.05 h and lower than or equal to 8 h,
- v. when step (b2) of the process is carried out in a continuous mode, a residence
15 time higher than or equal to 0.05 h and lower than or equal to 8 h.

20 15. Process according to any of claims 1 to 14 wherein the aqueous composition containing the organic substances to be treated originates from a process for manufacturing an epoxide, preferably from glycerol, or from a process for manufacturing a chlorinated organic compound, or from both processes.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/050982

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F1/76 C02F1/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

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PCT/EP2009/050982

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International application No

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